Cyclodextrins in the Emulsion Polymerization of Vinyl Monomers

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Summary

β-Cyclodextrin (CD) has been incorporated into emulsion polymerizations of vinyl monomers. Polymerizations of the sparingly soluble monomer, butyl methacrylate, were not affected by the presence of CD when a sulphonate cosurfactant was present. However, incorporation of CD into surfactant free polymerizations yielded stable latices in a formulation which gave a grossly coagulated product in the absence of CD. It was also found that the highly water insoluble monomers decyl and octadecyl methacrylate could be polymerized in emulsion if CD was added to the latex. In emulsion polymerization carried out in the absence of CD gross coagulation occurred early in the reaction. The role of CD in these systems appears to be solubilization of the hydrophobic monomers.

Introduction

Cyclodextrins (CDs) are well known cyclic species that can solubilize hydrophobic compounds in aqueous media.[1] The solubilization is effected by complexation of the water-insoluble species within the hydrophobic cavity of the CD. Heterogenous polymerizations, such as emulsion and suspension polymerizations, in which surfactants are essential components, are frequently used techniques for the preparation of high molecular weight polymers. These surfactants impart either electrostatic or entropic stability to the dispersion.[2] During our work on functional polymer colloids[3-5] we have surprisingly discovered that CD can also stabilize some polymer colloids in the absence of other conventional surfactants.[6,7] Successful emulsion polymerization requires the monomer to be partially water soluble so that highly hydrophobic monomers such as octadecyl methacrylate (OM) and dodecyl methacrylate (DM) cannot be homopolymerized in this way. We have however now discovered that both of these monomers can be homopolymerized in aqueous emulsion by using CD to transport the hydrophobic monomer into the aqueous phase. The following will report our work on the emulsion polymerization of a range of methacrylate monomers.

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Results

Addition of CD to an emulsion polymerization of BMA stabilized by sulphonate surfactant

Initially, CD was added to a sulphonate-stabilized (DPOS-45) emulsion polymerization of BMA. The formulations are given in table 1 (reactions 1,2,3). The effect on the rate of polymerization was negligible, all polymerizations being essentially complete after 30 minutes at 70 ° C. Also, little change in the final molecular weight average (Mn) or particle size was observed. From these observations it is then clear that, while β-CD may complex hydrophobes within this system, these complex structures have little effect on the course of the emulsion polymerization in the presence of sulphonate surfactant.

Table 1 Results of the emulsion polymerization of BMA

Ref	**BMA/g**	**Water /cm^{-3}**	**DPOS-45/g**	**CD/g**	**M$_n$/kg mol^{-1}**	**M$_w$/M$_n$**	**PS$^+$/nm**
1	80	200	1.7	0	673	3.2	120
2	80	200	1.7	0.4	532	3.4	105
3	80	200	1.7	1.6	622	3.0	107
4	80	200	0	0	31	8.3	coagulated
5	80	200	0	0.4	33	9.7	493
6	80	200	0	1.6	71	4.4	730
7	80	200	0	1.6	107	4.0	614
8	60	200	0	1.6	145	4.2	607
9	60	250	0	0.0	38	12.5	1000*
10	60	250	0	1.6	142	5.0	652
11	60	250	0	3.2	131	3.8	801
12	60	250	0	4.8	156	5.2	574
13	60	250	0	6.0	103	6.4	526

$^+$ Particle size

* Particle size of the latex, however 50% of the material was produced as coagulum

Addition of β-CD to a dispersion polymerization of BMA in the absence of surfactant

Following on from the above experiments, polymerizations were carried out in the absence of surfactant. The results for the various polymerization recipes are shown in table 1 (reactions 4-13). Initially a control polymerization was carried out. This reaction (reaction 4) contained neither surfactant nor CD and coagulated at an early stage in the polymerization. As can be clearly seen from these results, the addition of CD had a beneficial effect on the colloidal stability of the products. In reactions carried out at the monomer (solids) content of 28.5 % w/w. (reactions 5, 6 and 7), large amounts of product coagulated from the reaction mixture. However, unlike in the control experiment, a proportion of the polymer was present as a stable colloid. The fraction of polymer which was observed as a stable colloid was 25 and 70 % w/w, respectively, for reactions 5 and 6/7. An enhancement of the rate was inferred from the observation that at 0 and 1.8 mmol. dm^{-3} of aqueous phase the total amount of polymer formed after 300 minutes corresponded to approximately 15 % conversion of the monomer. Whereas, at the higher CD concentration of 7.1 mmol. dm^{-3} of aqueous phase, 75 % of the monomer had been converted in this time. Interestingly, the polymerizations carried out at a β -CD concentration of 7.1 mmol dm^{-3} of aqueous phase gave large regular particles of diameters circa 1mm as well as the smaller stable latex particles.

In the next set of polymerizations we attempted to minimize the amount of coagulum formed by reducing the solids content of the latex. The amount of material that was produced in colloidal form increased to values approaching 100% on reducing the solids content of the latices to approximately 19 % w/w. Thus, polymerizations 8-13 in table 1 gave latices that contained very little coagulum. As table 1 shows, all of these formulations gave latices with particle diameters circa 500 to 800 nm, with no clear relationship between CD concentration and particle size. Conversion time plots for some of these reactions are shown in figure 1.

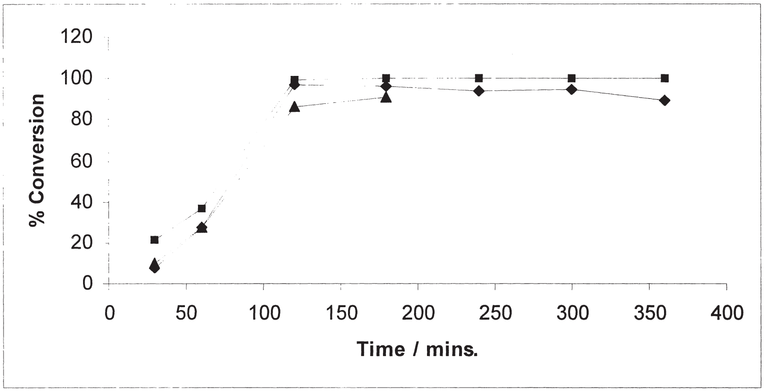

Figure 1 Conversion versus time plots for BMA polymerizations reactions in the presence of β-CD at β-CD concentrations of _◆5.64 mmol dm^{-3}, ■16.92 mmol dm^{-3}, ▲21.15 mmol dm^{-3}

It was also noticed that the storage stability of the latex increased with increasing CD concentrations; latices with lower CD concentrations displayed some settling over time whereas those with higher CD concentration remained well dispersed. Particle size distributions were either unimodal or, in some cases, bimodal. Molecular weight distributions were also unimodal with polydispersities between 4.0 and 6.5. Of note is the fact that these stable latices gave lower polydispersities and higher M_n than materials produced using the higher solids content and less stable formulations.

Polymerization of DM and OM in emulsion

As far as we were aware the homo emulsion polymerization DM and OM in the absence of excessive amounts of ionic surfactant had not been reported previously. Therefore we were prompted to attempt to use CDs in the emulsion polymerization of these highly hydrophobic monomers.

Table 2. The results of the characterization of the OM and DM latex preparations

Run.	**Monomer**	**CD/g**	**M_n /kg mol^{-1}**	**PD**	**Theoretical Solids /%**	**Coagulum /%**	**Average Particle size/nm**
1	DM	0.0	153	3.7	22	>50*	na
2	DM	1.5	183	5.4	22	33	278
3	DM	3.0	204	5.4	22	9	391
4	DM	6.0	235	4.9	22	3	591
5	DM	6.0	296	4.7	44	10	340
6	OM	6.0	283	3.6	22	18	330

(* Reaction 1 is a conventional preparation, more than 50% of the reaction mixture coagulated in the reaction vessel and the remaining monomer mixture phase separated on standing on the bench. Measurement conversion of conversion and particle were therefore not attempted.)

Initially a conventional emulsion polymerization was attempted with DM as the monomer, using a sulphonate (DPOS-45) surfactant system (reaction 1). This reaction produced over 50 % of the charged monomer in the form of coagulum. Whilst the rest of the polymer/monomer mixture that resulted was initially colloidally stable, the latex settled on standing on the bench. On addition of CD successful emulsion polymerization was achieved. Thus, in polymerizations 2, 3 and 4, which were all carried out at the same solids content as reactions 1 described above, stable latices resulted. The latices appeared to be indefinitely stable, that is they did not coagulate after 6 weeks standing on the bench at ambient temperature. However, in the case of polymerization 2 small amounts of coagulum did appear after 6 weeks. Conversions after 16 hours were very high but the polymerizations did not go to completion. SEC chromatograms showing also residual monomer are shown in figure 2. A final polymerization was carried out in which OM, another monomer that is very difficult, if not impossible, to homopolymerize by emulsion means, was examined. The final entry in table 1 shows the results from this polymerization. Inclusion of CD also produced a stable colloid of poly(octadecyl methacrylate) nanoparticles. The final conversion of monomer, however, was found to be slightly lower than in the similar DM polymerization.

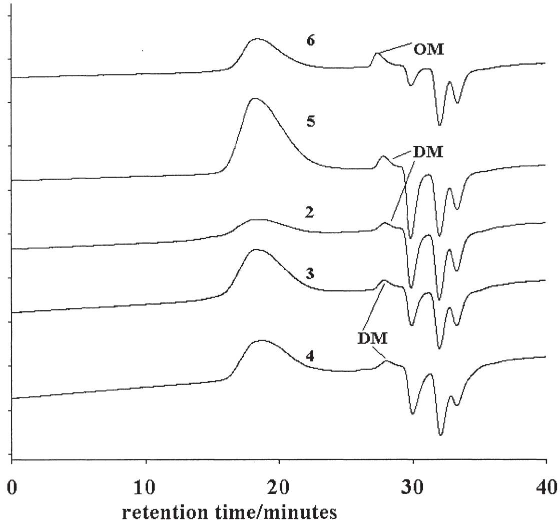

Figure 2 SEC chromatograms of polymerizations conducted in the presence of CD

Conclusion

In this work we have shown that CDs can have a role in the emulsion polymerization of vinyl monomers. The polymerization of sparingly water soluble monomers can be performed in water in absence of a cosurfactant and can yield high molecular material in latex form. Addition of CD to a sulphonate containing preparation had little effect on the molecular weight averages or the particle size and its distribution. CD is in these systems then able to provide colloidal stability by a mechanism, which at the current time has not been elucidated. In contrast to this behaviour the polymerization of the highly hydrophobic monomers OM and DM gave a stable latex only in the presence of sulphonate surfactant. The presence of CDs in these systems did however produce stable latices, which hitherto had been difficult if not impossible preparations. CD enhances the emulsion polymerization of these monomers by solubilization of the hydrophobes in water so that transfer of monomer into the aqueous phase is improved.

Experimental

A typical emulsion procedure was as follows:
Batch emulsion polymerizations of BMA were carried out. The ingredients minus the monomer were first charged to a flanged flask under a blanket of nitrogen. This mixture was then mechanically agitated at 70-C. The monomer and then potassium persulphate (0.5 g). was added through a dropping funnel. The conversion of monomer was established by determining the solid contents of samples of the latex. After 6-8 hours, the polymerization was terminated by cooling in ice. The latices were then filtered through glass wool and characterized by determining the average particle sizes, solids contents and molecular weights (by SEC).

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